

**Elemental Fractionation in Ultraviolet Laser Ablation of Igneous Silicate Minerals**

**Relevant to Mars**

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## ABSTRACT

Laser ablation has significant potential for terrestrial and extraterrestrial remote sampling applications if elemental fractionation can be understood and controlled. This study focuses on acmite, albite, augite, diopside, forsterite, and labradorite, silicate minerals that are relevant to Mars, Earth, the moon, and asteroids. The minerals were ablated using a frequency-quadrupled Nd:YAG laser (266 nm) and the ablation products were deposited as films on graphite substrates. Rutherford backscattering spectrometry and x-ray photoelectron spectroscopy measurements of the minerals and their films indicate Na, Mg, Si, Ca, and Fe fractionation effects. O fractionation effects were not observed. A simple cation replacement mechanism predicts fractionation effects that agree surprisingly well with the observed fractionation effects. These minerals can be easily distinguished by their film compositions despite the observed fractionation effects, indicating that ultraviolet laser ablation is feasible for sampling silicate minerals and is therefore potentially feasible for remote sampling applications.

## INTRODUCTION

Laser ablation is a technique that is often used to obtain vapor-phase material for subsequent chemical analysis [1-4]. Chemical information is obtained through either direct or indirect analysis of the ablation products. Direct approaches include optical spectroscopy and time-of-flight mass spectrometry [5-6]. In some indirect approaches, i.e. inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS), the ablation products are introduced into an additional excitation source [7-8]. In other indirect approaches the ablation products are deposited on a substrate, a process called pulsed laser deposition (PLD) [1-2]. The resulting films are analyzed by standard characterization techniques, i.e. Rutherford backscattering spectrometry (RBS) and x-ray photoelectron spectroscopy (XPS) [9-11].

Laser ablation is particularly feasible for chemical analysis of geological materials. It can be used to sample both conducting and insulating materials and is therefore applicable to a wide variety of rocks and minerals. Since extensive material preparation is not required, measurement time and opportunities for accidental contamination are minimal. Ablation crater diameters of a few tens of micrometers and ablation rates of a few nanometers per pulse are not atypical, facilitating both spatial profiling and depth profiling.

Fractionation in laser ablation has been studied for a variety of geological materials [12-14]. The majority of these studies used ICP-AES and ICP-MS techniques and focused on trace element fractionation. Photon absorption efficiency was found to vary from mineral to mineral, more significantly for infrared ablation and less significantly for ultraviolet ablation. Fractionation was found to correlate with absorbed

power density and to be more significant for infrared ablation than for ultraviolet ablation.

Fractionation attributed to laser ablation may arise in part from other sources. In ICP-AES and ICP-MS, for example, fractionation may occur during transport to the ICP or in the ICP. Recent ICP-MS measurements suggest that large particulates are often either lost during transport to the ICP or incompletely digested in the ICP and that this can result in fractionation [15-17].

Laser ablation has significant potential for terrestrial and extraterrestrial remote sampling applications if fractionation can be understood and controlled. This study was undertaken with that objective. A PLD approach rather than an ICP-AES or ICP-MS approach was selected to avoid potential fractionation arising from the ICP.

## **MINERAL SELECTION AND PREPARATION**

The Shergottite-Nakhlite-Chassignite (SNC) meteorites are believed to have originated on Mars and are reported to consist largely of feldspars, pyroxenes, and olivines [18]. The Earth's continental crust is reported to consist of 58% feldspars, 13% pyroxenes and amphiboles, and 3% olivines by volume [19]. These types of minerals are also relevant to the moon and asteroids. They are therefore of general interest for terrestrial and extraterrestrial remote sampling applications. The plagioclase feldspars albite and labradorite, the clinopyroxenes acmite, augite, and diopside, and the olivine forsterite were selected for this study. The nominal compositions of these minerals are shown in Table 1 [20].

All minerals used in this study are natural research-grade specimens obtained commercially [21]. Multiple specimens of each mineral were polished using silicon carbide films with average particulate diameters of 68  $\mu\text{m}$ , 22  $\mu\text{m}$ , and 14  $\mu\text{m}$  and diamond films with average particulate diameters of 6  $\mu\text{m}$ , 3  $\mu\text{m}$ , and 1  $\mu\text{m}$ .

## EXPERIMENTS

The experimental setup is shown in Figure 1. The ablation laser is a pulsed frequency-quadrupled Nd:YAG laser with an internal energy attenuator. The wavelength, pulse repetition rate, maximum pulse energy, and temporal pulse width are 266 nm, 15 Hz, 5 mJ, and 3-5 ns, respectively. The mineral target and the graphite substrate are separated by approximately 2.5 cm and are housed in a vacuum chamber with a typical pressure of  $5 \times 10^{-8}$  Torr. The laser is focused to approximately  $0.4 \text{ mm}^2$  at the target surface. Prior to ablation, the average powers incident on the target and reflected from the target are measured using a thermopile meter. During ablation, the position of the target is adjusted at intervals of 4500 pulses to provide a fresh target area. Ablation is stopped when a film is visible on the substrate.

Films were deposited from acmite, albite, augite, diopside, and forsterite targets at nominal power densities of  $100 \text{ MWcm}^{-2}$  and  $320 \text{ MWcm}^{-2}$  and from a labradorite target at a nominal power density of  $320 \text{ MWcm}^{-2}$ . A nominal power density of  $100 \text{ MWcm}^{-2}$  was insufficient to achieve a visible ablation plume in the case of labradorite. These nominal power densities were calculated assuming a temporal pulse width of 4 ns and a spatial area of  $0.4 \text{ mm}^2$ . This power density varied slightly due to variations in target reflectivity arising from composition and surface roughness.

## CHARACTERIZATION

In RBS the sample is irradiated with monochromatic ions [9-11]. The ions undergo Coulomb repulsion collisions with the sample atoms and are backscattered. The energy loss of each backscattered ion is determined by the penetration depth and the mass and the density of the sample atoms and is relatively independent of the chemical environments of the sample atoms. The effective sampling depth is typically a micrometer. The RBS system used in this study produces a beam of 2 MeV  $\text{He}^{2+}$  ions with a sampling area of approximately  $25 \text{ mm}^2$ .

In XPS the sample is irradiated with monochromatic x-rays [9-10]. The sample atom electrons absorb the x-rays and are ejected. The energy of each ejected electron is determined by the electron binding energy and is a function of the sample atoms and their chemical environments. The effective sampling depth is limited by the escape depth of the ejected electrons and is typically several nanometers. Because XPS has a small effective sampling depth, surface contamination may affect results. Samples are often exposed to an ion beam just prior to characterization to sputter-clean their surfaces. The XPS system used in this study produces a focused beam of 1486.6 eV Al  $K\alpha$  x-rays with a sampling area of approximately  $0.3 \text{ mm}^2$  for characterization and a beam of  $\text{Ar}^+$  ions for removal of surface contamination.

RBS was selected as the primary characterization technique for this study because large sampling depth, large sampling area, and insensitivity to chemical environment make RBS preferable to XPS for mean composition measurements. All targets and films were characterized by RBS and selected targets and films were characterized by XPS. Ablated targets were polished prior to characterization to eliminate material potentially

affected by the ablation process. To evaluate the variations in composition between and within targets, two targets of each mineral were characterized by RBS and one target of each mineral was characterized by RBS, polished, and characterized again by RBS. To remove surface contamination 5 nm of material was sputtered from the surfaces of targets and films characterized by XPS. This was found to be less effective for the targets than for the films, possibly because of shadowing effects arising from greater surface roughness. For the targets, five areas within the sputtered area were characterized to compensate for variations in composition arising from surface contamination.

## **RESULTS**

To demonstrate the ability of RBS to accurately indicate composition, a specimen of NIST 1830 was polished and characterized. Table 2 shows the composition indicated by NIST and the composition obtained from a fit to the RBS spectrum. The uncertainty shown for the latter composition is the two-sigma uncertainty in the fit. For each element the value indicated by RBS agrees with the value indicated by NIST to within the uncertainty in the RBS value.

Table 3(a) shows the compositions indicated by RBS for the targets and films. For all of the minerals variations in composition between targets were not significant in comparison to variations in composition within a target. Each target composition is the mean of three compositions obtained from fits to spectra collected from multiple targets and the uncertainty shown is the two-sigma uncertainty in the mean. Each film composition was obtained from a fit to a spectrum and the uncertainty shown is the two-sigma uncertainty in the fit. RBS is unable to distinguish between Al and Si in the albite

and labradorite films and is therefore able to provide accurate Al+Si values but unable to provide accurate Al and Si values for those films. Figures 2(a) and 2(b) show the Na, Mg, Si, Al+Si, Ca, and Fe values indicated by RBS for the targets and films. For all of the minerals the O film values agree with the O target values to within the sum of the uncertainties in the values. The O film values were therefore set equal to the O target values in order to minimize error arising from normalization.

Table 3(b) shows the compositions indicated by XPS for the targets and films. Each film composition was obtained from a fit to a spectrum and the uncertainty shown is the two-sigma uncertainty in the fit. Each target composition is the mean of five compositions obtained from fits to spectra collected from multiple areas on a target and the uncertainty shown is the two-sigma uncertainty in the mean. In XPS the O signals are unstable for the targets, possibly due to surface contamination or preferential sputtering, and XPS is therefore unable to provide accurate O values for the targets.

The compositions indicated by RBS and XPS differ slightly. These deviations are not atypical and most likely occur because elemental sensitivity varies with factors such as chemical environment. In this study the relative compositions of the targets and films are of interest and therefore the differences in the compositions indicated by the two techniques are not relevant.

To clearly identify fractionation effects the ratios  $R_1$  and  $R_2$

$$R_1 = (F - T) / T$$

$$R_2 = (F - T) / (f + t)$$

were calculated for Na, Mg, Si, Al+Si, Ca, and Fe using the RBS data shown in Table 3(a). F is the film value, T is the target value, f is the uncertainty in the film value, and t

is the uncertainty in the target value. As in Figures 2(a) and 2(b) the O film values were set equal to the O target values in order to minimize error arising from normalization. Negative  $R_1$  and  $R_2$  values indicate depletion effects and positive  $R_1$  and  $R_2$  values indicate enrichment effects.

The  $R_1$  and  $R_2$  values are shown in Table 4 and Figures 3(a) and 3(b). An  $R_2$  value with an absolute value greater than unity indicates a significant fractionation effect. Both acmite films are depleted in Na and the film deposited at the higher power density is enriched in Ca. Both albite films are depleted in Ca and enriched in Na. Both augite films are depleted in Fe and the film deposited at the higher power density is enriched in Ca. Both diopside films are enriched in Ca, the film deposited at the lower power density is depleted in Mg, and the film deposited at the higher power density is depleted in Si and Fe. Both forsterite films are depleted in Mg and the film deposited at the higher power density is enriched in Fe. The labradorite film is neither depleted nor enriched in any of the elements. XPS confirms these fractionation effects in the films for which data is available.

## **DISCUSSION**

Potential sources of fractionation include laser-target interactions, laser-vapor interactions, vapor-vapor interactions, and vapor-substrate interactions. A comprehensive investigation of these interactions and their potential fractionation effects are beyond the scope of this study. However, a rudimentary effort was made to develop a simple theory consistent with the observed fractionation effects in order to predict the behavior of laser ablation in its context as a sampling technique for geological materials.

Ablation occurs when the incident power density is equal to or greater than a threshold power density that varies with parameters including laser wavelength and material composition. At a lower power density thermal desorption and laser desorption can occur. The minerals used here were exposed to an incident power density that varied with position and time for each pulse. The ablation rates, estimated from measurements of film volume and adjusted to compensate for loss of material between the target and the substrate, were on the order of a nm per pulse. Prior to ablation a large fraction of the surface material was exposed to an incident power density lower than the threshold. Consequently there was opportunity for desorption to occur.

Fractionation effects observed in previous studies have been attributed to thermal and laser conditioning of the target surface [7,12,22]. Similarly, the fractionation effects observed in this study may arise from a cation replacement mechanism triggered by thermal desorption, laser desorption, or other processes. In the first step species that are characterized by weak bonds are preferentially released from lattice sites. In the second step species that are characterized by strong bonds are preferentially captured by empty lattice sites. Since desorbed species typically lack the energy and directionality of ablated species and are less likely to arrive at the substrate, the second step can potentially occur at the target surface, at the film surface, or at both surfaces.

The minerals used here are characterized by a tetrahedral structural unit comprised of a central  $\text{Si}^{4+}$  cation bonded to four  $\text{O}^{2-}$  anions [19,23]. The  $\text{O}^{2-}$  anions in these structural units bond to additional cations to compensate for charge imbalance. In olivines the tetrahedrons are isolated and the structural unit is  $\text{SiO}_4^{4-}$ . In clinopyroxenes two  $\text{Si}^{4+}$  share every other  $\text{O}^{2-}$  and the structural unit is  $\text{SiO}_3^{2-}$ . In plagioclase feldspars

two  $\text{Si}^{4+}$  share every  $\text{O}^{2-}$  and the structural unit is  $\text{SiO}_2$ .  $\text{Al}^{3+}$  is substituted for  $\text{Si}^{4+}$  in one quarter to one half of the tetrahedrons to produce  $\text{AlO}_2^-$ .

There are three cation site types in clinopyroxenes, the tetrahedral ( $\text{P}_0$ ) sites, small sites ( $\text{P}_1$ ) with six-fold coordination, and large sites ( $\text{P}_2$ ) with eight-fold coordination [19,23]. These sites occur in a 2:1:1 ratio. The compositions of the clinopyroxenes used here indicate that the set of cations available to fill these sites is comprised of  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Si}^{4+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Fe}^{3+}$ . The  $\text{P}_0$  sites are believed to be occupied by  $\text{Si}^{4+}$  and by  $\text{Fe}^{3+}$  in the absence of sufficient  $\text{Si}^{4+}$ . In clinopyroxenes in which  $\text{P}_0$  sites are occupied by only one type of cation with a 4+ charge state, as here, the  $\text{P}_1$  and  $\text{P}_2$  sites are occupied by cations with a 2+ charge state [19,23]. In clinopyroxenes of this type the accepted assignment order of cations to the  $\text{P}_1$  and  $\text{P}_2$  sites is  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Ca}^{2+}$  [23]. The  $\text{P}_1$  sites are believed to be occupied by  $\text{Mg}^{2+}$  and  $\text{Fe}^{2+}$  and by  $\text{Ca}^{2+}$  in the absence of sufficient  $\text{Mg}^{2+}$  and  $\text{Fe}^{2+}$  in accordance with the accepted order. The larger  $\text{P}_2$  sites are believed to be occupied by  $\text{Ca}^{2+}$  and by  $\text{Fe}^{2+}$  and  $\text{Na}^+$  in the absence of sufficient  $\text{Ca}^{2+}$ . This change in the order reflects a possible preference of the  $\text{P}_2$  sites for cations with large radii, i.e.  $\text{Ca}^{2+}$  and  $\text{Na}^+$ . The  $\text{P}_2$  sites in many natural clinopyroxenes are typically occupied by  $\text{Ca}^{2+}$  and  $\text{Na}^+$  [19,23].

There are three cation site types in olivines, the tetrahedral ( $\text{O}_0$ ) sites and two sites ( $\text{O}_1$  and  $\text{O}_2$ ) with six-fold coordination [19,23]. These sites occur in a 1:1:1 ratio. The composition of the olivine used here indicates that the set of cations available to fill these sites is comprised of  $\text{Mg}^{2+}$ ,  $\text{Si}^{4+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Fe}^{3+}$ . The  $\text{O}_0$  sites are believed to be occupied by  $\text{Si}^{4+}$  and by  $\text{Fe}^{3+}$  in the absence of sufficient  $\text{Si}^{4+}$ . The  $\text{O}_1$  and  $\text{O}_2$  sites are occupied by cations with a 2+ charge state [19,23]. The accepted order for assignment of cations to

the  $O_1$  and  $O_2$  sites is  $Mg^{2+}$  and  $Fe^{2+}$  [23]. The  $O_1$  and  $O_2$  sites are believed to be occupied by  $Mg^{2+}$  and  $Fe^{2+}$  in accordance with the accepted order.

There are two cation site types in plagioclase feldspars, the tetrahedral ( $F_0$ ) sites and sites ( $F_1$ ) with six-fold or seven-fold coordination [19,23]. These sites occur in a 4:1 ratio. The compositions of the plagioclase feldspars used here indicate that the set of cations available to fill these sites is comprised of  $Na^+$ ,  $Al^{3+}$ ,  $Si^{4+}$ ,  $Ca^{2+}$ ,  $Fe^{2+}$ , and  $Fe^{3+}$ . The  $O_0$  sites are believed to be occupied by  $Si^{4+}$  and by  $Al^{3+}$  and  $Fe^{3+}$  in the absence of sufficient  $Si^{4+}$ . The  $F_1$  sites are occupied by cations with a 1+ or 2+ charge state [19,23]. The accepted order for assignment of cations to the  $F_1$  sites is a function of the cations occupying the  $F_0$  sites and is determined by charge state [23]. Replacement of  $Al^{3+}$  or  $Fe^{3+}$  by  $Si^{4+}$  in  $F_0$  sites is coupled to replacement of  $Ca^{2+}$ ,  $Mg^{2+}$ , or  $Fe^{2+}$  by  $Na^+$  in  $F_1$  sites. The  $F_1$  sites are believed to be occupied by  $Ca^{2+}$  and  $Na^+$  and by  $Fe^{2+}$  in the absence of sufficient  $Ca^{2+}$  and  $Na^+$  in accordance with the accepted order.

The placement of a cation in the assignment order for a site type is a reflection of the relative bond strength between the cation and the site type and can be used to predict fractionation effects introduced by a cation replacement mechanism. In the clinopyroxenes used here the predicted effects are replacement of  $Fe^{3+}$  by  $Si^{4+}$  in  $P_0$  sites, replacement of  $Ca^{2+}$  by  $Mg^{2+}$  and  $Fe^{2+}$  in  $P_1$  sites, and replacement of  $Fe^{2+}$  and  $Na^+$  by  $Ca^{2+}$  in  $P_2$  sites. In the olivine used here the predicted effects are replacement of  $Fe^{3+}$  by  $Si^{4+}$  in  $O_0$  sites. In the plagioclase feldspars used here the predicted effects are replacement of  $Al^{3+}$  and  $Fe^{3+}$  by  $Si^{4+}$  in  $F_0$  sites and replacement of  $Ca^{2+}$  and  $Fe^{2+}$  by  $Na^+$  in  $F_1$  sites. Since  $Mg^{2+}$  and  $Fe^{2+}$  have the same charge state and similar radii, significant

replacement of  $\text{Fe}^{2+}$  by  $\text{Mg}^{2+}$  in  $\text{P}_1$  sites in the clinopyroxenes and in  $\text{O}_1$  and  $\text{O}_2$  sites in the olivine is not expected.

Tables 5(a), 5(b), and 5(c) show the estimated distributions of cations in sites for the clinopyroxene, olivine, and plagioclase feldspar targets. Cation ratios were calculated from the RBS data shown in Table 3(a). Cations were then assigned to sites based on the site ratios, cation ratios, and assignment orders. Tables 5(a), 5(b), and 5(c) also show the estimated distributions of cations in sites after the cation replacement mechanism has taken effect. The final distributions for the clinopyroxenes and olivine are assumed to be those which would occur if the cation replacement mechanism proceeded to completion. In the plagioclase feldspars charge balance requires that complete replacement of  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  by  $\text{Si}^{4+}$  in  $\text{F}_0$  sites be coupled to complete elimination of cations from the  $\text{F}_1$  sites. Therefore the final distribution for the plagioclase feldspars is assumed to be that which would occur if the cation replacement mechanism proceeded until the  $\text{Si}^{4+}:\text{Al}^{3+}$  ratio in  $\text{F}_0$  sites is at the maximum value consistent with complete occupancy of  $\text{F}_1$  sites.

Tables 4 and 6 show  $R_1$  values for Na, Mg, Al, Si, Al+Si, Ca, and Fe in acmite, albite, augite, diopside, forsterite, and labradorite. The experimental values, shown in Table 4, were calculated from the RBS data shown in Table 3(a). The theoretical values, shown in Table 6, were calculated from the cation distributions shown in Tables 5(a), 5(b), and 5(c). In Table 7 the elements are shown in order of increasing  $R_1$  value for each mineral. Elements with identical experimental  $R_1$  values are shown in order of increasing  $R_2$  value. The cation replacement mechanism correctly predicts [Fe, Mg, Si, Ca] for augite and diopside and [Fe, Ca, Al+Si, Na] for labradorite. For albite it correctly predicts [Ca, Al+Si] but incorrectly predicts the placement of [Na]. For forsterite it correctly

predicts [Mg, Si] but incorrectly predicts the placement of [Fe]. For acmite it correctly predicts [Na, Mg, Ca] and [Na, Fe, Si] but incorrectly predicts the relative placements of [Mg, Ca] and [Fe, Si].

The cation replacement mechanism proposed here is too simple to predict fractionation effects to a high degree of accuracy. Replacement of  $\text{Mg}^{2+}$  and  $\text{Fe}^{2+}$  by  $\text{Fe}^{3+}$  and replacement of  $\text{Fe}^{2+}$  by  $\text{Mg}^{2+}$  in  $\text{P}_1$  sites in clinopyroxenes and in  $\text{O}_1$  and  $\text{O}_2$  sites in olivines may occur [23].  $\text{Fe}^{2+}$  shows a slight preference for  $\text{O}_1$  sites in some olivines, suggesting that replacement of  $\text{Mg}^{2+}$  by  $\text{Fe}^{2+}$  may occur [23]. These effects and others were neglected for the sake of simplicity and for the lack of sufficient physical data. Nonetheless, the predicted fractionation effects agree surprisingly well with the observed fractionation effects. It should be noted that the placement of [Fe] in the experimental values for forsterite and the relative placements of [Mg, Ca] and [Fe, Si] in the experimental values for acmite are not self-consistent. The incorrect predictions for forsterite and acmite should be considered in that context.

## CONCLUSIONS

Acmite, albite, augite, diopside, forsterite, and labradorite are silicate minerals comprised of Na, Mg, Al, Si, Ca, and Fe cations and O anions. No O fractionation effects were observed. Na depletion and Ca enrichment in acmite, Ca depletion and Na enrichment in albite, Fe depletion and Ca enrichment in augite, Mg, Si, and Fe depletion and Ca enrichment in diopside, and Mg depletion and Fe enrichment in forsterite were observed. A simple cation replacement mechanism predicts fractionation effects that agree surprisingly well with the observed fractionation effects.

These minerals can be easily distinguished by their film compositions despite the observed fractionation effects. These results are of interest because they indicate that ultraviolet laser ablation is a feasible technique for sampling silicate minerals and is therefore a potentially feasible technique for a variety of terrestrial and extraterrestrial remote sampling applications.

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## FIGURE CAPTIONS

Figure 1: Ablation/deposition system.

Figure 2: Compositions in atomic percents as indicated by RBS for the films deposited at (a) low and (b) high power densities. The values are displaced along the horizontal axis for ease of display. Where no fractionation is observed the values lie on the indicator lines.

Figure 3:  $R_1$  and  $R_2$  values calculated from the RBS data in Table 3(a) for films deposited at (a) low and (b) high power densities. The O film values were set equal to the O target values in order to minimize error arising from normalization. Each symbol represents Na (up triangle), Mg (square), Si or Al+Si (circle), Ca (down triangle), or Fe (diamond) in acmite (solid), albite (open), augite (—), diopside (|), forsterite (+), or labradorite (x).

Table 1: Silicate minerals selected for this study [20].

Mineral	Classification	Nominal Composition
Acmite	Clinopyroxene	$\text{NaFeSi}_2\text{O}_6$
Albite	Plagioclase Feldspar	$\text{NaAlSi}_3\text{O}_8$
Augite	Clinopyroxene	$(\text{Ca},\text{Na})(\text{Mg},\text{Fe})\text{Si}_2\text{O}_6$
Diopside	Clinopyroxene	$\text{CaMgSi}_2\text{O}_6$
Forsterite	Olivine	$\text{Mg}_2\text{SiO}_4$
Labradorite	Plagioclase Feldspar	30% $\text{NaAlSi}_3\text{O}_8$ 70% $\text{CaAl}_2\text{Si}_2\text{O}_8$

Table 2: NIST 1830 compositions  
in atomic percents as indicated by  
NIST and RBS.

Element	NIST	RBS
O	60.5	$60.7 \pm 1.7$
Na	9.2	$9.2 \pm 0.7$
Mg	2.0	$1.8 \pm 0.6$
Si	25.2	$25.0 \pm 0.6$
Ca	3.2	$3.3 \pm 0.1$

Table 3(a): Compositions in atomic percents as indicated by RBS for the targets (upper) and the films deposited at low (center) and high (lower) power densities.

Element	Acmite	Albite	Augite	Diopside	Forsterite	Labradorite
O	$59.1 \pm 1.5$	$62.1 \pm 0.2$	$59.6 \pm 1.0$	$59.9 \pm 0.3$	$57.2 \pm 0.8$	$61.9 \pm 0.8$
	$58.2 \pm 1.4$	$62.0 \pm 2.8$	$60.2 \pm 2.3$	$60.4 \pm 2.3$	$57.4 \pm 1.6$	—
	$59.1 \pm 0.9$	$60.9 \pm 1.7$	$57.6 \pm 1.0$	$58.2 \pm 1.4$	$57.3 \pm 1.6$	$61.2 \pm 1.9$
Na	$4.7 \pm 1.0$	$7.7 \pm 0.3$	—	—	—	$2.7 \pm 1.1$
	$2.6 \pm 0.3$	$9.2 \pm 0.6$	—	—	—	—
	$2.7 \pm 0.2$	$9.4 \pm 0.5$	—	—	—	$3.5 \pm 0.3$
Mg	$4.6 \pm 1.3$	—	$7.6 \pm 0.2$	$10.0 \pm 0.4$	$25.7 \pm 0.1$	—
	$4.6 \pm 0.3$	—	$7.6 \pm 0.5$	$8.9 \pm 0.5$	$24.3 \pm 0.8$	—
	$4.4 \pm 0.3$	—	$7.6 \pm 0.2$	$9.6 \pm 0.4$	$24.5 \pm 0.8$	—
Al	—	$6.3 \pm 1.2$	—	—	—	$12.0 \pm 1.3$
	—	—	—	—	—	—
	—	—	—	—	—	—
Si	$19.3 \pm 1.5$	$23.5 \pm 0.9$	$19.2 \pm 0.3$	$19.9 \pm 0.3$	$13.9 \pm 0.8$	$18.4 \pm 1.2$
	$21.4 \pm 0.5$	—	$19.5 \pm 0.7$	$19.1 \pm 0.7$	$15.0 \pm 0.5$	—
	$20.5 \pm 0.3$	—	$20.3 \pm 0.3$	$19.6 \pm 0.5$	$14.8 \pm 0.5$	—
Al + Si	—	—	—	—	—	—
	—	$28.7 \pm 1.0$	—	—	—	—
	—	$29.6 \pm 0.8$	—	—	—	$30.4 \pm 0.7$
Ca	$6.6 \pm 0.7$	$0.4 \pm 0.0$	$9.1 \pm 0.8$	$9.1 \pm 0.2$	—	$4.8 \pm 0.2$
	$7.0 \pm 0.2$	$0.1 \pm 0.1$	$9.4 \pm 0.3$	$10.8 \pm 0.4$	—	—
	$7.8 \pm 0.2$	$0.1 \pm 0.1$	$10.8 \pm 0.2$	$11.8 \pm 0.3$	—	$4.8 \pm 0.1$
Fe	$5.7 \pm 0.3$	—	$4.5 \pm 0.3$	$1.1 \pm 0.2$	$3.2 \pm 0.1$	$0.2 \pm 0.0$
	$6.2 \pm 0.1$	—	$3.3 \pm 0.1$	$0.8 \pm 0.1$	$3.3 \pm 0.1$	—
	$5.5 \pm 0.1$	—	$3.7 \pm 0.1$	$0.8 \pm 0.1$	$3.4 \pm 0.1$	$0.1 \pm 0.1$

Table 3(b): Compositions in atomic percents as indicated by XPS for the targets (upper) and the films deposited at high power densities (lower).

Element	Acmite	Albite	Augite
O	61.31 $61.31 \pm 0.35$	61.53 $61.53 \pm 0.31$	62.16 $62.16 \pm 0.32$
Na	$2.39 \pm 0.68$ $1.58 \pm 0.04$	$3.52 \pm 0.41$ $8.88 \pm 0.09$	— —
Mg	$3.48 \pm 0.96$ $3.93 \pm 0.15$	— —	$5.13 \pm 0.32$ $5.62 \pm 0.16$
Al	— —	$8.05 \pm 0.25$ $8.26 \pm 0.19$	— —
Si	$20.42 \pm 0.68$ $20.41 \pm 0.27$	$25.89 \pm 0.82$ $21.20 \pm 0.25$	$21.17 \pm 0.49$ $19.45 \pm 0.24$
Ca	$7.03 \pm 1.67$ $8.72 \pm 0.15$	$1.01 \pm 0.09$ $0.13 \pm 0.02$	$7.69 \pm 0.81$ $10.24 \pm 0.15$
Fe	$5.37 \pm 0.32$ $4.05 \pm 0.05$	— —	$3.85 \pm 0.26$ $2.53 \pm 0.04$

Table 4:  $R_1$  and  $R_2$  values calculated from the RBS data in Table 3(a) for films deposited at low (upper) and high (lower) power densities. The O film values were set equal to the O target values in order to minimize error arising from normalization.

Element	Function	Acmite	Albite	Augite	Diopside	Forsterite	Labradorite
Na	$R_1$	-0.46 -0.43	0.19 0.18	— —	— —	— —	— 0.27
	$R_2$	-1.66 -1.67	1.64 1.76	— —	— —	— —	— 0.53
Mg	$R_1$	-0.02 -0.04	— —	0.01 -0.05	-0.10 -0.08	-0.05 -0.04	— —
	$R_2$	-0.06 -0.13	— —	0.16 -0.90	-1.10 -0.99	-1.42 -1.27	— —
Si	$R_1$	0.08 0.06	— —	0.03 0.01	-0.03 -0.06	0.08 0.07	— —
	$R_2$	0.82 0.67	— —	0.59 0.23	-0.56 -1.38	0.91 0.72	— —
Al + Si	$R_1$	— —	-0.04 -0.04	— —	— —	— —	— -0.02
	$R_2$	— —	-0.38 -0.38	— —	— —	— —	— -0.17
Ca	$R_1$	0.04 0.18	-0.75 -0.75	0.05 0.13	0.20 0.24	— —	— -0.02
	$R_2$	0.28 1.33	-3.00 -3.00	0.40 1.19	3.07 4.44	— —	— -0.30
Fe	$R_1$	0.06 -0.04	— —	-0.26 -0.22	-0.26 -0.30	0.04 0.07	— -0.50
	$R_2$	0.93 -0.50	— —	-2.88 -2.43	-0.97 -1.10	0.60 1.05	— -1.00

Table 5(a): Estimated distributions of cations in the clinopyroxenes before (upper) and after (lower) the cation replacement mechanism has taken effect.

Site Type	Cation	Acmite	Augite	Diopside
P <sub>0</sub>	Si <sup>4+</sup>	47.19	47.52	49.62
		50.00	50.00	50.00
	Fe <sup>3+</sup>	2.81	2.48	0.38
		0.00	0.00	0.00
P <sub>1</sub>	Mg <sup>2+</sup>	11.25	18.82	24.94
		12.57	18.82	24.94
	Fe <sup>2+</sup>	11.13	6.18	0.06
		12.43	6.18	0.06
P <sub>2</sub>	Ca <sup>2+</sup>	2.62	0.00	0.00
		0.00	0.00	0.00
	Ca <sup>2+</sup>	13.52	22.52	22.70
		25.00	25.00	25.00
	Fe <sup>2+</sup>	0.00	2.48	2.30
		0.00	0.00	0.00
	Na <sup>+</sup>	11.48	0.00	0.00
		0.00	0.00	0.00

Table 5(b): Estimated distributions of cations in the olivine before (upper) and after (lower) the cation replacement mechanism has taken effect.

Site Type	Cation	Forsterite
O <sub>0</sub>	Si <sup>4+</sup>	32.48 33.33
	Fe <sup>3+</sup>	0.85 0.00
O <sub>1</sub> & O <sub>2</sub>	Mg <sup>2+</sup>	60.04 60.04
	Fe <sup>2+</sup>	6.63 6.63

Table 6:  $R_I$  values calculated from the estimated cation distributions in Tables 5(a), 5(b), and 5(c).

Element	Acmite	Albite	Augite	Diopside	Forsterite	Labradorite
Na	-1.00	-0.02	—	—	—	1.82
Mg	0.12	—	0.00	0.00	0.00	—
Al	—	—	—	—	—	—
Si	0.06	—	0.05	0.01	0.03	—
Al + Si	—	0.02	—	—	—	0.00
Ca	0.55	-1.00	0.11	0.10	—	-1.00
Fe	-0.11	—	-0.45	-0.98	-0.11	-1.00

Table 7: The elements in order of increasing  $R_1$  value. The experimental orders, calculated from the  $R_1$  values in Table 4, are for films deposited at low (upper) and high (lower) power densities. The theoretical orders were calculated from the  $R_1$  values in Table 6.

Mineral	Theoretical Order	Experimental Order
Acmite	Na Fe Si Mg Ca	Na Mg Ca Fe Si Na Fe Mg Si Ca
Albite	Ca Na Al+Si	Ca Al+Si Na Ca Al+Si Na
Augite	Fe Mg Si Ca	Fe Mg Si Ca Fe Mg Si Ca
Diopside	Fe Mg Si Ca	Fe Mg Si Ca Fe Mg Si Ca
Forsterite	Fe Mg Si	Mg Fe Si Mg Si Fe
Labradorite	Fe&Ca Al+Si Na	— Fe Ca Al+Si Na









